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Wu et al. J Agric Food Chem (1991), vol. 39, no. 1, pp. 170-172

Tokitomo et al. Agric Biol. Chem. (1984), vol. 48, no. 11, pp. 2869-70

Nicholas. Phytochemistry (1973), vol. 2, pp. 381-399

Nagnan et al. Oleagineux (1992), vol. 47, no. 3, pp. 135-42

Umano et al. J. Agric. Food Chem. (1992), vol. 40, no. 4, pp. 599-603

Gunawardena. J. Natl. Sci. Counc. Sri Lanka (1994), vol. 22, no. 3, pp. 231-238

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Miscellaneous Volatile Plant Products

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When freshly cut plant parts are steam-distilled, the distillate on condensation usually yields an oily product known as an "essential oil," the term indicating that the fragrant "essence" of the plant has been obtained. The history of the origin and development of the production of essential oils has been comprehensively surveyed by Guenther (1959). In time, the procurement of plant "essences" included the *enfleurage* method, whereby fragrant plant products were for all practical purposes "extracted" at room temperature over a period of time by contact with odorless fats (although the process does entail in addition an actual fermentation in some cases). Later the use of solvent extraction and distillation of the solvent to leave an oily residue was introduced. All three methods produce essential oils. When terpenes are present, steam distillation produces largely monoterpenes, although some sesquiterpene hydrocarbons are obtained in the distillate also. The *enfleurage* process and solvent extraction produce not only monoterpenes, but also numerous oxygenated compounds of all classes. Essential oils, therefore, may consist of an extraordinarily complex mixture of compounds. It is still not generally recognized that any of the three methods may produce in the final product a

large number of compounds *completely unrelated structurally to the terpenes*. It will be the purpose of this chapter to emphasize the diverse nature of the products other than terpenes, to suggest that the term "essential oil" be divorced from the term "terpenes," and that the term essential oil be used only in the interest of describing the *fragrance* of the plant—to whatever this fragrance may be due. The odor or fragrance of a plant (e.g., the *Alliums*) may be completely unrelated to its terpene content, and in the same context a plant may be rich in a particular terpene which by itself is odorless (e.g., the diterpene sclareol in *Salvia sclarea*). "Essential oils" may even contain such diverse substances as *n*-undeca-1,3,5-triene(s) (Naves, 1967) and phthalides (Stahl and Bohrmann, 1967).

In this chapter no specific distinction has been made between the various methods of isolation (i.e., steam distillation, enfleurage, and solvent extraction).

FREE ACIDS

Probably all plants contain some degree of free acid which can be volatilized by steam or extracted with organic solvents. Fatty acids up to caproic (C_6) are volatile with steam and can be isolated by steam distillation. Caprylic acid (C_8) and capric acid (C_{10}) are slightly volatile with steam, but, as Robinson (1967) has pointed out, require long periods of distillation for complete removal. On the other hand, some essential oils obtained by means other than steam distillation contain higher molecular weight fatty acids such as palmitic and stearic. Some examples of free "fatty" acids isolated from plant tissue in more recent years are given in Table 10.1. Particularly noteworthy is the complexity of the mixture obtained from *Juniperus turkestanica* essential oil, which yielded acids from acetic (C_2) to tridecylic (C_{30}). In summary, volatile acids from C_2 to C_{10} can be obtained from plant tissues. Extraction methods may also isolate fatty acids and even branched acids of relatively high molecular weight.

FREE ALIPHATIC ALCOHOLS

All of the straight chain alcohols up to C_{10} have been found in plants as free alcohols. In addition some branched chain alcohols have been detected. Some examples from the recent literature are given in Table 10.2. They are most frequently saturated, but unsaturated forms are occasionally found (e.g., (–)-1-octene-3-ol (Table 10.2). According to Robinson (1967), odd- as well as even-numbered alcohols occur frequently. Secondary alcohols as well as

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Table 10.1 Some Free Fatty Acids Detected in Plant Isolates.

<i>Aliphatic Acids</i>	<i>Plant Source</i>	<i>Reference</i>
acetic	<i>Elsholtzia ciliata</i>	Fujita et al. (1967)
senecioic	"	"
isovaleric	tobacco flowers	Kapetanovic (1965), Fujita et al. (1967)
isocaprylic	"	Fujita et al. (1967)
caprylic	"	"
palmitic	raspberry juice, press cake	Bohnsack (1967)
stearic	"	"
caprylic	tobacco flowers	Kapetanovic (1965)
acetic	<i>Juniperus turkestanica</i> essential oil	Goryaev et al. (1967a)
propionic	"	"
butyric	"	"
caproic	"	"
isoeanthic	"	"
isocaprylic	"	"
isodecanoic	"	"
dodecanoic	"	"
undecanoic	"	"
lauric	"	"
isolauric	"	"
tridecylic	"	"
myristic	"	"
formic	noble laurel essential oil	Goryaev et al. (1967b)
acetic	"	"
propionic	"	"
caproic	"	"
eanthic	mandarin oil	D'Amore and Calabro (1966)
caprylic	"	"
pelargonic	"	"
capric	"	"
undecanoic	"	"
dodecanoic	"	"

primary are also rather common, but they usually have their hydroxyl groups at C-2, and never farther along the chain than C-3. Aliphatic alcohols up to C₁₃ in chain length are readily steam-distillable, and as with acids, continued steam distillation would probably remove alcohols up to C₁₈ in chain length.

Alcohols and their corresponding ketones and aldehydes often occur simultaneous in fruits, berries, and vegetables (Eriksson, 1968). This is probably due to the activity of the enzyme alcohol : NAD oxidoreductase

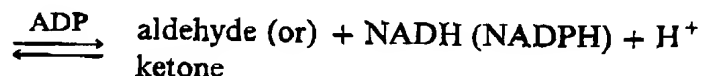
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Table 10.2 Some Fermentable Aliphatic Alcohols Detected in Plant Isolates.

Aliphatic Alcohol	Plant Source	Reference
3-octanol	<i>Elsholtzia ciliata</i>	Fujita et al. (1967)
ethanol	tobacco flowers	Kapetanovic (1965)
methanol	soybean	Arai et al. (1967)
ethanol	"	"
2-pentanol	"	"
isopentanol	"	"
n-pentanol	"	"
n-hexanol	"	"
n-heptanol	"	"
hexanol	lavender and lavandin oils	Peyron and Benezet (1966)
ethanol	apples	Paillard (1967)
butanol	"	"
(-)-1-octene-3-ol	<i>Psalliotia campestris</i>	Freytag and Ney (1968)
methanol	apples	Katayama et al. (1966)
isopropyl alcohol	"	"
ethanol	"	"
propanol	"	"
isobutyl alcohol	"	"
butanol	"	"
isopentanol	"	"
pentanol	"	"
hexanol	"	"
decyl alcohol	summer orange essential oil	Kadota and Nakamura (1967)
2-methylbut-3-en-2-ol	hops	Hartley and Fawcett (1967)
trans-2-methyl-6-methylene-3,7-octadien-2-ol	<i>Juniperus ashei</i>	von Rudloff (1968)

(E. C. 1.1.1.1.), which introduces an equilibrium between an alcohol and its corresponding aldehyde or ketone according to the reaction:

primary (or)
secondary } alcohol + NAD⁺ (NADP⁺)



The stoichiometry of this enzyme has been studied in the seeds and pods of the pea plant, *Pisum sativum* (Eriksson, 1968).

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ALIPHATIC ESTERS

Next to the more fragrant terpenes, aliphatic esters are probably more widely responsible for characteristic plant odors than any other volatile chemical constituents. For example, it appears that the characteristic aroma of Bartlett pear essence is due to the methyl and ethyl esters of *trans-2-cis-4-decadienoic*

Table 10.3 Some Aliphatic Esters Isolated From Plant Tissues.

<i>Aliphatic Esters</i>	<i>Plant Source</i>	<i>Reference</i>
isobutyl valerate	<i>Elsholtzia</i> essential oil	Fujita et al. (1967)
acetyl palmitate	raspberry juice	Bohnsack (1967)
stearyl acetate	"	"
methyl heptanoate	Brewer's Gold hops oil	Buttery et al. (1965)
methyl-4-methyl hexanoate	"	"
methyl-5-methyl hexanoate	"	"
2-methyl butyl-2- methyl butyrate	"	"
hexyl acetate	lavender and lavandin oils	Peyron and Benezet (1966)
3-octyl acetate	"	"
3-octenyl acetate	"	"
1-hexyl butyrate	"	"
3-octenyl butyrate	"	"
<i>n</i> -hexyl butanoate	"	"
amyl acetate	apples	Paillard (1967)
butyl butyrate	"	"
ethyl acetate	"	"
butyl acetate	"	"
ethyl butyrate	"	Katayama et al. (1966)
butyl acetate	"	"
methyl formate	"	"
isoamyl acetate	"	"
ethyl caproate	"	"
cetyl acetate	mandarin oil	D'Amore and Calabro (1966)
nonyl acetate	"	"
decyl acetate	"	"
undecyl acetate	"	"
<i>n</i> -pentanol acetate	soybean	Arai et al. (1967)
Me(CH ₂) ₄ -CH- EtOAc	<i>Elsholtzia ciliata</i>	Fujita et al. (1967)
octanol esters (undefined)	<i>Heracleum sosnowsky</i> oil	Sedzik et al. (1966)

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Table 10.4 Aliphatic Aldehydes and Their Plant Sources Recently Detected in Plant Tissues

<i>Aliphatic Aldehydes</i>	<i>Plant Source</i>	<i>Reference</i>
acetaldehyde	tea	Gogiya and Motsonelidze (1965)
isobutyric aldehyde	"	"
isovaleric aldehyde	"	"
caproic aldehyde	"	"
acetaldehyde	apples, pears, grapes, currants	Pribela (1966)
formaldehyde	tea (incompletely fermented)	Skobeleva 1966)
acetaldehyde	"	"
propionaldehyde	"	"
butyraldehyde	"	"
isobutyraldehyde	"	"
valeraldehyde	"	"
isovaleraldehyde	"	"
caproaldehyde	"	"
acetaldehyde	apples	Katayama et al. (1966)
propionaldehyde	"	"
2-hexen-1-al	mandarin oil	D'Amore and Calabro (1966)
furfural	"	"
heptenal	"	"
octanal	"	"
nonanal	"	"
decanal	"	"
undecanal	"	"
dodecanal	"	"
caprylaldehyde	summer orange	Kadota and Nakamura (1967)
furfural	chin-chin, catnip oils	Montes (1967)
formaldehyde	<i>Cryptomonas ovata</i> var. <i>palustris</i> (an algae)	Collins and Kalnins (1966)
acetaldehyde	"	"
valeraldehyde	"	"
heptanal	"	"
decanal	summer orange essential oil	Kadota and Nakamura (1967)

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caproic aldehyde	"	"
acetaldehyde	apples, pears, grapes, currants	Pribela (1966)
formaldehyde	tea (incompletely fermented)	Skobeleva 1966)
acetaldehyde	"	"
propionaldehyde	"	"
butyraldehyde	"	"
isobutyraldehyde	"	"
valeraldehyde	"	"
isovaleraldehyde	"	"
caproaldehyde	"	"
acetaldehyde	apples	Katayama et al. (1966)
propionaldehyde	"	"
2-hexen-1-al	mandarin oil	D'Amore and Calabro (1966)
furfural	"	"
heptenal	"	"
octanal	"	"
nonanal	"	"
decanal	"	"
undecanal	"	"
dodecanal	"	"
caprylaldehyde	summer orange	Kadota and Nakamura (1967)
furfural	chin-chin, catnip oils	Montes (1967)
formaldehyde	<i>Cryptomonas ovata</i> var. <i>palustris</i> (an algae)	Collins and Kalnins (1966)
acetaldehyde	"	"
valeraldehyde	"	"
heptanal	"	"
decanal	summer orange essential oil	Kadota and Nakamura (1967)

Table 10.5 Some Aliphatic Ketones Detected in Plant Tissues.

Compound	Plant Source	Reference
2-heptanone	endoconidium-forming fungi	Collins and Kalnins (1966)
1,2-cyclopentandione	coffee oil	Walter and Weidemann (1967)
6,9-pentadecadien-2-one	oil from Brewer's Gold hops	Buttery et al. (1965)
2-propanone	<i>Cryptomonas ovata</i>	Collins and Kalnins (1966)
ethyl amyl ketone	lavender and lavandin oils	Peyron and Benezet (1966)
methyl heptenone	mandarin oil	D'Amore and Calabro (1966)

Robinson "phenols are usually not steam distillable, but phenol ethers or esters, being less polar than the parent hydroxyl compounds, can often be distilled with steam." Certainly, however, the more simple phenols like phenol itself and catechol are steam-distillable. "Coumarin is customarily isolated by steam distillation," according to Robinson (1967). 1,4-Quinones (as opposed to the 1,2-quinones), which have semiphenolic properties, are often steam-distillable; in fact this characteristic, with additional testing, provides a partial means of identification (Robinson, 1967, p. 53). Thus the complexity of compounds that might occur in a steam-distillable fraction is increased.

It seems unlikely that the chromones (e.g., khellin) will be steam-distillable,

Table 10.6 Some Phenols (Aromatic Alcohols) Recently Isolated from Plants.

Aromatic Alcohols	Plant Source	Reference
β -phenylethyl alcohol	rose water	Rollet et al. (1967)
"	raspberry juice	Bohnsack (1967)
"	rose	Borikhina et al. (1965)
<i>p</i> -hydroxybenzyl alcohol	mustard (incubated)	Kawakishi and Muramatsu (1966)
"	Bourbon vanilla pods	Bohnsack and Seibert (1965)
<i>p</i> -hydroxybenzaldehyde	"	"
benzyl alcohol	raspberry	Bohnsack (1965)
(-)-epicatechol	<i>Camelia japonica</i>	Bohnsack (1967); Nakagawa and Sakamoto (1967)
(+)-catechol	"	Nakagawa and Sakamoto (1967)

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but they can readily be extracted from dried plant material with ether, chloroform, or similar polar solvents. Similarly, flavonoids and related compounds can be expected to be present in a plant extract prepared with polar solvents like ethanol, acetone, and so on, but they are not likely to be present in steam distillates. On the other hand, most of the coumarins may be expected in steam-distilled isolates (e.g., umbelliferone, psoralen, and so on) (Reyes and Gonzalez, 1966). The structural diversity of compounds that may exist in this category is shown in Figure 10.1. A few phenolic compounds isolated from plants in recent years, along with their plant source, are presented in Table 10.6. It should be borne in mind that these substances can, and frequently do, exist in plant tissues as esters and ethers, thereby also contributing to characteristic plant essence (e.g., anisaldehyde, anisic acid, and so forth, in aniseed oil) (Zacsko-Szasz and Szasz, 1966). Table 10.7 illustrates the complexity of certain plant tissues (e.g., *Citrus* sp.) with respect to their content of phenols or closely related products.

Table 10.7 Coumarins, Flavones, and Related Products in Essences of Lemon, Bergamot, Tangerine, Bitter Orange, and Sweet Orange*.

<i>Compound</i>	<i>Compound</i>
5-hydroxypsoralen	5,6,7,8,3',4'-hexamethoxyflavone
8-(2,3-dihydroxy-3-methylbutoxy)-5-methoxypsoralen	5,6,7,8,4'-pentamethoxyflavone, Me anthranilate
5,7-dimethoxycoumarin	Me <i>N</i> -methylantranilate
8-geranyloxypsoralen	5,8-dihydroxy-3,7,3'4'- tetramethoxy-flavone
5-geranyloxy-7-methoxycoumarin	
5-geranyloxypsoralen	7-geranyloxycoumarin
	7-hydroxycoumarin
	5-methoxypsoralen
	5-isopentenylloxypsoralen

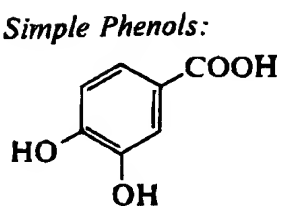
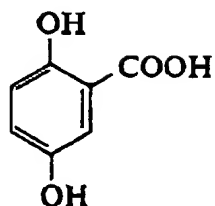
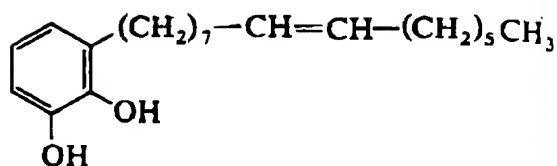
* From D'Amore and Calapaj (1965).

MISCELLANEOUS NITROGEN AND SULFUR COMPOUNDS

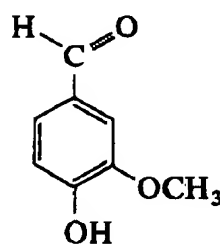
Many amines and sulfur compounds are obtained from plant tissue by steam distillation or distillation of solvent extracts, in the case of amines if the macerated tissue medium is on the alkaline side. For a complete discussion, including possible biosynthetic mechanisms, the reader is referred to Robinson, Chapter 14 (1967). Volatile amines may include isopentylamine

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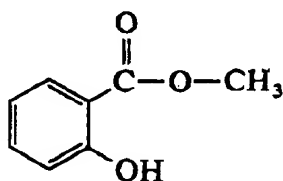
Simple Phenols:

Protocatechuic Acid
(*allium* spp.)Gentisic Acid
(*theobroma cacao*)Urushiol (*Rhus* spp.)

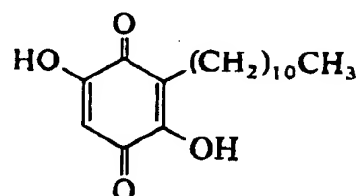
Benzoquinones:



Vanillin

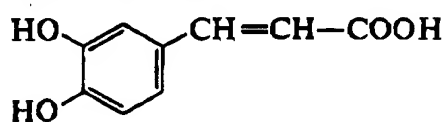


Methyl Salicylate

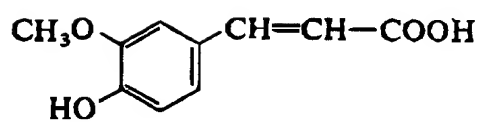


Embelin

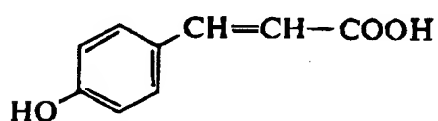
Phenylpropanes:



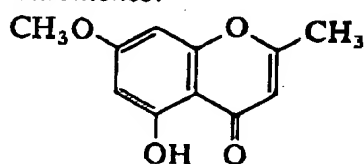
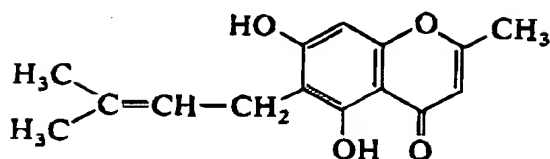
Caffeic Acid



Ferulic Acid

*p*-Coumaric Acid

Chromones:

Eugenin
(*Eugenia caryophyllata*)Peucenin
(*Peucedanum ostruthium*)

Anthraquinones:

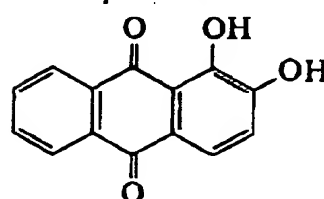
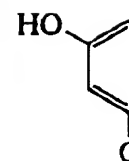
Alizarin
(*Rubia tinctorum*)

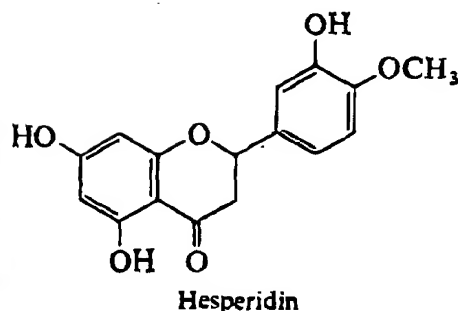
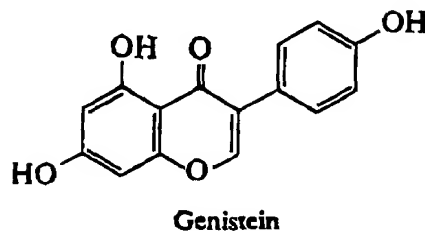
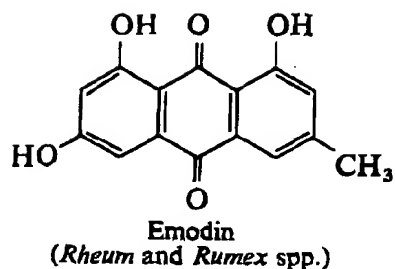
Figure 10.1 Miscellaneous phenolic compounds from plant tissues.

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*Flavonoids and Related
Compounds:*



Coumarins:

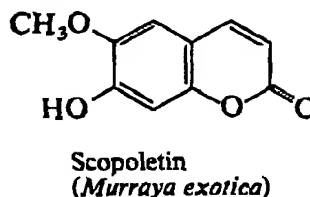
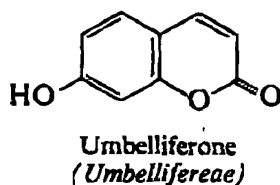
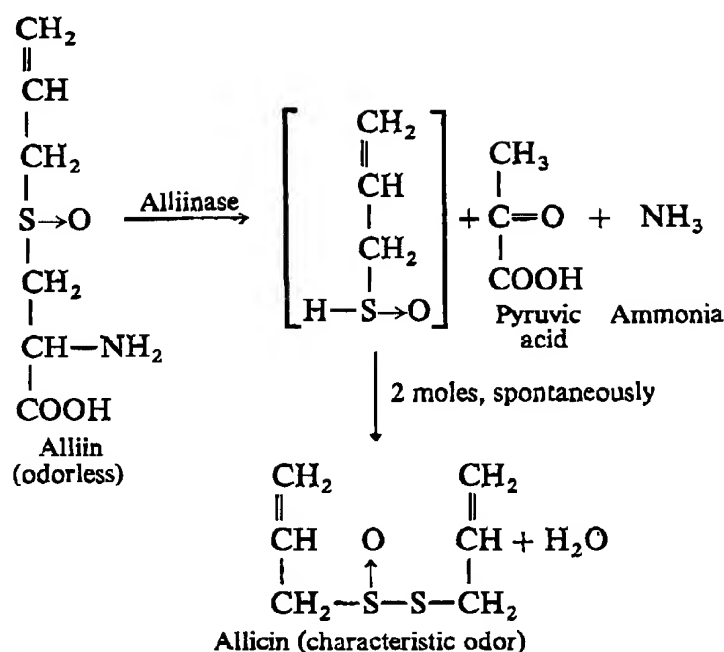


Figure 10.1 (continued)

$\text{H}_3\text{C}-\text{CH}(\text{H}_3\text{C})-\text{CH}_2-\text{CH}_2\text{NH}_2$. which is widespread in occurrence among

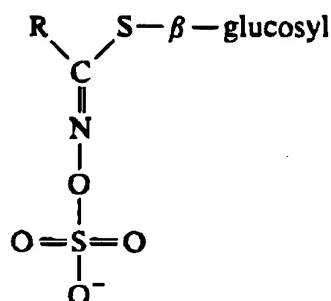
plants, and methylamine and trimethylamine. Dimethylamine is rare in occurrence (see von Kamienski, 1957, for review). The mercaptans (RSH) and monosulfides ($\text{R}-\text{S}-\text{R}'$) are volatile, but it is possible that disulfides ($\text{R}-\text{S}-\text{S}-\text{R}$) may be found in steam distillates also. It may be generally assumed that an unpleasant odor in plants is due to an amine or sulfur compound such as a thiol or sulfide. Methyl mercaptan is found in radish roots, and 2,2'-dithioisobutyric acid and the corresponding disulfide are found in asparagus, and probably account for unpleasant odors in breath and urine (respectively) found after eating these plant roots. Amines account for the repulsiveness to man and attractiveness to insects exhibited by aroids (Smith and Meeuse, 1966). Volatile amines present in apples are presumably formed biosynthetically by transamination of preformed aldehydes (Hartmann, 1967).

The characteristic odor of garlic and onion (*Allium* species) is due in large part to the formation of the disulfide allicin, by enzymatic action on alliin when the plant is crushed (Figure 10.2). Allium is a general name for several possible substrates which may give rise, through enzymatic action, to alllicins. According to Bernhard (1968), a typical alliin, e.g., S-allylcysteine sulfoxide, on treatment with the enzyme allinase gives rise to allicin, e.g., diallyl thiosul-

Figure 10.2 The formation of allicin in *Allium* species (after Robinson, 1967).

finite. The allïcins, however, are unstable and in addition to being highly odoriferous themselves, decompose (on heating or, more slowly, spontaneously) to equally odoriferous constituents. The complexity of the allium odor problem has been emphasized by Bernhard (1968), who found that the principal disulfide present in fresh "Sunspice" onions was di-*n*-propyl, followed (in order of decreasing amount) by *n*-propyl allyl, methyl-*n*-propyl, methyl allyl, dimethyl, and diallyl disulfides. A carbon-sulfur lipase capable of decomposing allïins in the *Allium* genus has also been found in *Tulbaghia*, a genus of South African origin which contains species described as having garliclike odors (Jacobsen et al., 1968).

Some "mustard oils" are volatile and odoriferous and may be isolated by steam distillation. These oils occur in plants in the form of mustard oil glycosides having the general formula:



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The sugar unit (usually glucose) may be removed by macerating the plant tissues in H_2O for several hours to permit hydrolysis by the enzyme myrosinase. The nonsugar (aglucon) portion usually undergoes rearrangement, so that one may obtain isothiocyanates ($RN=C-S$), thiocyanates ($RSCN$), nitriles (RCN), or an N-substituted thiourethane ($RN=C-OR'$) (see Robinson, 1967, for review). Most of the mustard oils themselves are liquids with a sharp, irritating odor, and some can raise blisters when placed on the skin. Typical plants containing mustard oils are mustard (seed), horseradish, and water cress; the characteristic flavor and taste of these plants is attributed to mustard oils. Figure 10.3 shows the structural formulas for some volatile mustard oils. Some miscellaneous sulfur compounds and their plant sources cited in recent literature are given in Table 10.8 (see also Volume I, Chapter 11 and Volume III, Chapter 2).

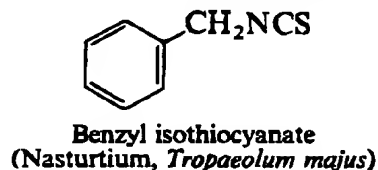
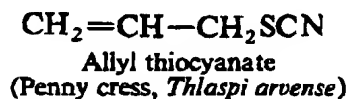
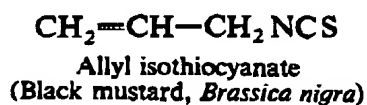


Figure 10.3 Some volatile mustard oils (after Robinson, 1967).

Table 10.8 Miscellaneous Sulfur Compounds.

Compound	Plant Source	Reference
3-butenyl isothiocyanate	rapeseed oil	Young and Wetter (1967)
4-pentenyl isothiocyanate	"	"
isothiocyanate	rapeseed	Trzebny (1967)
thioxazolidone	"	"
methyl thiohexanoate	oil from Brewer's Gold hops	Buttery et al. (1965)
isothiocyanate	white mustard paste	Kawakishi and Muramatsu (1966)
β -phenyl isothiocyanates	Japanese horseradish	Kojima et al. (1966)
vinyl thioxazolidones	rapeseed	Grajewska and Kruszewska (1967)

MISCELLANEOUS VOLATILE PLANT ESSENCES

It has been recognized for a number of years that the typical aroma of many fruits is due to a major volatile chemical constituent. The following compounds and their associated plant odors are characteristic: vanillin (vanilla), methyl salicylate (wintergreen), piperonal (heliotrope), cinnamaldehyde (cinnamon), eugenol (cloves), apiol (parsley, celery), and methyl anthranilate (grapes). It is also becoming evident, however, that the more abundant constituents do not necessarily give the *true*, subtle aroma of the fruit. The advent of gas chromatography and mass spectrometry has made it evident that minor constituents also play an important role in contributing to essence value. Some examples will now be given since they represent the complexity that volatile material other than terpenes can present in plant tissues. Many of these constituents are steam-distillable.

Apple Essence

About forty constituents have been identified or suggested to be present in the volatile flavoring matter of apples (Schultz et al., 1967). These consist largely

Table 10.9 Major Apple Essences.

<i>Essence Extracted</i>	<i>Recovery*</i>
ethanol	49
1-propanol	19
isobutanol	12
1-butanol	120
2-methylbutan-1-ol	140
1-hexanol	195
<i>trans</i> -2-hexen-1-ol	61
acetaldehyde	trace
hexanal	66
<i>trans</i> -2-hexenal	295
ethyl acetate	56
ethyl propionate	7
propyl acetate	11
ethyl butyrate	13
butyl acetate	61
2-methylbutyl acetate	43
hexyl acetate	18
<i>trans</i> -2-hexenyl acetate	10

* Mg. from 1 Kg. of 150-fold aqueous essence. See Schultz et al. (1967) for further details.

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of aliphatic alcohols, aldehydes, and esters. In a recent investigation several different solvents were used for extraction. The materials extracted and relative recovery with ethyl ether as the solvent are shown in Table 10.9. The two major constituents were a C_6 aldehyde and alcohol respectively. (See also Katayama et al., 1966; Paillard, 1967.)

Grape Essence

As previously mentioned the characteristic odor of the Concord grape is due primarily to the methyl ester of anthranilic acid, as has been known since 1921 (Power and Chestnut, 1921). In a recent investigation (Stern et al., 1967) sixty components were identified, some of them having been recorded also by previous investigation. These are shown in Table 10.10. Esters represented the largest percentage of components, with methyl anthranilate and ethyl acetate predominating. Particularly interesting were some crotonate esters, unusual for plant extracts.

Table 10.10 Components of Concord Grape Essence.*

<i>Compound</i>	<i>Compound</i>	<i>Compound</i>
isopentane	ethyl crotonate	isobutylbenzene
ethanol	2-hexanol	methylpropylbenzene
2-methylpentane	<i>p</i> - and/or <i>m</i> -xylene	1,2,3-trimethylbenzene
3-methylpentane	furfural	ethyl hex-2-enoate
hexane	isopropyl crotonate	alkylbenzene
ethyl acetate	hex-3-ene-1-ol	acetophenone
2-methyl-3-buten-2-ol	hexanol	methoxyphenol
methylcyclopentane	<i>O</i> -xylene	linalool
isopropyl acetate	hex-2-en-1-ol	ethyl alkylthioester
cyclohexane	ethyl pentanoate	ethyl β -hydroxy-
ethyl propionate	isopropylbenzene	hexanoate
<i>n</i> -propyl acetate	<i>n</i> -propylbenzene	ethyl benzoate
methyl butyrate	<i>m</i> -ethyltoluene	indole
diethoxyethane	<i>p</i> -ethyltoluene	terpinene-4-ol
4-methyl-2-pentanone	1,3,5-trimethylbenzene	α -terpineol
ethyl isobutyrate	benzaldehyde	methyl benzyl acetate
methyl crotonate	<i>O</i> -ethyltoluene	methyl anthranilate
toluene	ethyl hexanoate	ethyl anthranilate
hexanol	1,2,4-trimethylbenzene	
ethyl butyrate	isobutyl crotonate	

* Stern et al., 1967

VOLATILE COMPOUNDS OF AMERICAN CRANBERRY (*V. MACROCARPON* AIT.)

One does not think of the cranberry as a particularly odiferous fruit, yet it does have a characteristic aroma. In a recent investigation forty-two compounds comprising over 95% of the aroma complex were identified (Croteau and Fagerson, 1968) in the juice of the American cranberry. Aromatic compounds (benzaldehyde, benzyl and benzoate esters) and several monoterpenes (α -terpineol, β -pinene, linalool, etc.) appeared to be the major contributors to American cranberry aroma. The compounds identified are shown in Table 10.11. A number of these have also been identified in American cranberry "press cake" (Anjou and von Sydow, 1967).

Table 10.11 Volatile Compounds Identified in
Cranberry Juice.*

Compound	Percentage of Concentrate
Aromatic	
benzene(s)	.1
benzaldehyde	9.6
benzyl ethyl ether	1.0
acetophenone	.8
methyl benzoate	1.0
benzyl formate	.7
ethyl benzoate	1.0
benzyl acetate	.7
benzyl alcohol	6.0
2-phenyl ethanol	2.2
4-methoxy benzaldehyde	.8
2-hydroxy diphenyl	1.2
benzyl benzoate	11.9
dibutyl phthalate(s)	1.1
Terpenes	
alpha-pinene	.1
beta-pinene	.2
myrcene	.2
limonene	1.1
linalool	.6
alpha-terpineol	13.0
nerol	1.1
Aliphatic alcohols	
2-methyl-3-buten-2-ol	.9
2-pentanol	.8
pentanol	.9
hexanol	.7

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Table 10.11 (continued)

Compound	Percentage of Concentrate
1-octen-3-ol	.8
octanol	2.3
nonanol	.8
decanol	.7
octadecanol	.8
Aliphatic aldehydes	
acetaldehyde(s)	.1
pentanal	.2
hexanal	.8
octanal	.9
nonanal	1.0
decanal	.8
Other compounds	
diacetyl	.3
ethyl acetate	.7
2-furaldehyde	.8
methyl heptanoate	.6
Acids	
benzoic acid	26.6
2-methylbutyric acid	.3
Total	95.2

* From Croteau and Fegerson, 1968.

Table 10.12 Volatile Components of Pineapple.*

Compound
acetoxyacetone
methyl β -hydroxybutyrate
dimethylmalonate
trans-tetrahydro- α,α -5-trimethyl-5-vinyl furfuryl alcohol
methyl <i>cis</i> -(4?)-octenoate
γ -butyrolactone
methyl β -hydroxyhexanoate
ethyl β -hydroxyhexanoate
methyl β -acetoxyhexanoate
ethyl β -acetoxyhexanoate
γ -octalactone
δ -octalactone

* From Creveling et al. (1968).

VOLATILE COMPONENTS OF PINEAPPLE (*ANNANAS COMOSUS* L.)

An investigation of the volatile constituents of pineapple has added twelve constituents to those already known to contribute to the strong, characteristic aroma of pineapple (Creveling et al., 1968). These are shown in Table 10.12. They include the γ - and δ -octalactones, which exhibit a coconut-like aroma, the unusual tetrahydro- α,α -*l*-trimethyl-*l*-vinyl furfuryl alcohol, and several β -hydroxy esters, which have a rather repulsive odor.

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